CAVITATION REACTION ENGINEERING

The Plenum *Chemical Engineering Series*

Series Editor:

Dan Luss, *University of Houston, Houston, Texas*

CAVITATION REACTION ENGINEERING

Y. T. Shah, A. B. Pandit, and V. S. Moholkar

COAL COMBUSTION AND GASIFICATION

L. Douglas Smoot and Philip J. Smith

ENGINEERING FLOW AND HEAT EXCHANGE, Revised Edition

Octave Levenspiel

INDUSTRIAL CRYSTALLIZATION: Process Simulation Analysis and Design

Narayan S. Taware

REACTION ENGINEERING OF STEP GROWTH POLYMERIZATION

Santosh K. Gupta and Anil Kumar

THE STRUCTURE AND REACTION PROCESSES OF COAL

K. Lee Smith, L. Douglas Smoot, Thomas H. Fletcher, and Ronald J. Pugmire

TRANSPORT MECHANISMS IN MEMBRANE SEPARATION PROCESSES

J. G. A. Bitter

A Continuation Order Plan is available for this series. A continuation order will bring delivery of each new volume immediately upon publication. Volumes are billed only upon actual shipment. For further information please contact the publisher.

CAVITATION REACTION ENGINEERING

Y. T. Shah

*Clemson University
Clemson, South Carolina*

and

A. B. Pandit and V. S. Moholkar

*University of Bombay
Bombay, India*

Springer Science+Business Media, LLC

Library of Congress Cataloging-in-Publication Data

Shah, Yatish T.

Cavitation reaction engineering / Y.T. Shah, and A.B. Pandit,
and V.S. Moholkar.

p. cm. -- (Plenum chemical engineering library)

Includes bibliographical references and index.

1. Cavitation. 2. Chemical processes. I. Pandit, A.B.
II. Moholkar, V.S. III. Title. IV. Series

TP156.C38S48 1999

660'.284--dc21

99-37362

CIP

ISBN 978-1-4613-7168-7

ISBN 978-1-4615-4787-7 (eBook)

DOI 10.1007/978-1-4615-4787-7

© 1999 Springer Science+Business Media New York

Originally published by Kluwer Academic / Plenum Publishers in 1999

Softcover reprint of the hardcover 1st edition 1999

10 9 8 7 6 5 4 3 2 1

A C.I.P. record for this book is available from the Library of Congress.

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form
or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise,
without written permission from the Publisher

To James, Keith, Jonathan, and Heather
Y.T.S.

PREFACE

The literature on cavitation chemistry is ripe with conjectures, possibilities, heuristic arguments, and intelligent guesses. The chemical effects of cavitation have been explained by means of many theories, consisting of empirical constants, adjustable parameters, and the like. The chemists working with cavitation chemistry agree that the phenomenon is very complex and system specific. Mathematicians and physicists have offered partial solutions to the observed phenomena on the basis of cavitation parameters, whereas chemists have attempted explanations based on the modes of reaction and the detection of intermediate chemical species. Nevertheless, no one has been able to formulate a unified theme, however crude, for its effects on the basis of the known parameters, such as cavitation and transient chemistry involving extremely high temperatures of nanosecond durations.

When one surveys the literature on cavitation-assisted reactions, it is clear that the approach so far has been “Edisonian” in nature. While a large number of reactions have showed either enhanced yields or reduced reaction times, many reactions have remained unaffected in the presence of cavitation. The success or failure of cavitation reactions ultimately depends on the collapse of the cavity.

Cavitation chemistry is based on the principles of the formation of small transient cavities, their growth and implosion, which produce chemical reactions caused by the generation of extreme pressures and temperatures and a high degree of micro-turbulence. Cavities can be generated either by expansion of pressure (caused hydrodynamically or acoustically) or by sharp penetration of energy by lasers or protons. This monograph deals with the reaction engineering associated with the cavitation phenomenon and its practical applications in the treatment of various types of aqueous waste or for organic synthesis.

Mathematical modeling of cavitation phenomena and the related chemical effects is rather complex; even for the simplest reactions, there appears no possibility of a generalized theory in the near future. The chemical effects observed and reported in the literature as either transient or time averaged most definitely have resulted from the cavitation phenomenon. All researchers and a few practitioners will not

have any difficulty in accepting newly coined terms of cavitation chemistry and cavitation reaction engineering, which encompasses all aspects of the chemical transformations caused by the cavitation phenomenon.

This monograph is an attempt to present the observed effects on a common basis, namely, the parameters affecting cavitation, those affecting chemistry, and those affecting both, which are important in an appropriate design of a cavitation reactor. The mathematical modeling of cavitation bubble dynamics, chemical reactions, and reactors is discussed, with an emphasis on the physical explanations of the phenomena on the basis of known parameters affecting cavitation or parameters affecting the chemical transformations and the performance of the reactors.

The cavitation process can be categorized according to the method used to produce cavities. Hydrodynamic cavitation is produced by the pressure variation in a flowing liquid that is caused by the variation of velocity in the system. At the points of highest velocity and lowest pressure, cavities can occur. These cavities can (1) move with the liquid and subsequently collapse (i.e., traveling cavitation); (2) remain fixed at a rigid surface under unsteady state condition (i.e., fixed cavitation); or (3) reside in the cores of vortices (i.e., vortex cavitation) that form in the regions of high shear and boundary layer separation. Traveling cavitation is most efficient for chemical conversion. Acoustic cavitation is produced by sound waves in a liquid that are caused by pressure variations. Optical cavitation is produced by a laser light rupturing the liquid. Finally, particle cavitation is produced by the deposition of energy using any other type of elementary particle, such as a proton.

Chapter 1 briefly discusses the underlying physics behind the sources of cavitation. Instruments are currently available to produce cavities from these different sources. Cavitation bubbles and their behavior under different environments form the basis for how the cavitation process affects chemical transformation.

A suitable mathematical description of bubble dynamics and their interaction with the surrounding liquid medium is given in Chapter 2. While a complete description of bubble behavior is rather complex, the mathematics outlined in this chapter form the basis upon which more complex models can be developed. The modifications of the equations and the incorporation of the parameters involving physical effects are presented for different modes of cavitation. Different types of cavitation are discussed on the basis of the mode of energy dissipation and the time scales involved for this energy dissipation. The similarities and differences arising are discussed as part of a unified theme of energy dissipation and conversion for cavitation.

Finally, the physical parameters that affect the nature of the process in each type of cavitation are described in Chapter 3. The relationship between the physical parameters and the nature of the cavitation behavior described in this chapter is qualitatively and in some instances quantitatively obtained from an evaluation of the basic equations for cavitation bubble dynamics.

The success or failure of cavitation-assisted reactions ultimately depends on the active or reactive species generated as a result of cavity collapse. The cavitation phenomenon consists of three stages: nucleation, growth, and collapse of a single cavity or a cluster of cavities. A scientific approach to cavitation chemistry requires the control of these three stages.

Although nucleation is a fairly random phenomenon, considerable control over the rate has been achieved in the crystallization process by controlling the degree of supersaturation (metastable region) or by the addition of external nuclei (seeding). It may be possible to do the same for the nucleation of cavities or a cluster of cavities. Growth and collapse behavior of the cavity or the cluster of cavities is controlled by the surrounding fluctuating pressure field, i.e., its frequency and amplitude. Since the generation of active and reactive species depends on this cavity behavior, the success or failure of the reaction is related to the frequency and amplitude of the surrounding pressure field.

It is expected that from Chapters 1–3, the reader will be made aware of the common underlying theme responsible for a variety of chemical effects reported in the literature. The reader will also become conversant with cavitation as a physical phenomenon and the factors affecting this physical phenomenon. Where there is no literature on an experimental proof of the physical phenomena predicted by the mathematical and physical equations, numerical predictions have been used liberally to explain cavitation-related physical effects. This involves the behavior of a single cavity or a cluster of cavities in a variety of surroundings; i.e. form, mode, and time scales of energy dissipation.

Cavitation can have beneficial effects on a reaction as a result of physical effects such as microstreaming or chemical effects such as generation of OH^- radicals (hydrolysis or oxidative reactions). Control of these effects requires a fundamental analysis of cavity dynamics and not a simple use of cavitation intensity, as is often done in the literature. In Chapters 4 and 5 on gas–liquid cavitation chemistry and gas–liquid–solid cavitation chemistry, an attempt has been made to relate or use the predicted and observed physical effects of cavitation to explain the chemical and physical transformations observed and reported in the literature. Wherever possible, the parameters responsible for the chemical transformations and the changes in these parameters as a result of the physical phenomena of cavitation are highlighted. Heterogeneous cavitation chemistry and homogeneous cavitation chemistry, which are incorrectly separated in the literature, are presented on a common footing here because cavitation chemistry is always heterogeneous (more than one phase) owing to the formation of vapor- or gas-filled cavities. The correct separation is indicated in the titles of these two chapters.

Various possible and suggested mechanisms of cavitation-aided practical chemical reactions are also briefly discussed in Chapters 4 and 5. The interesting behavior of a variety of chemical reactions in the presence of cavitation is illustrated with the support of the experimental facts. The emphasis is largely on chemical trans-

formations in the aqueous phase so that the results are useful in treating aqueous waste. The mode of generation of the cavitation, its physical effect, and its ultimate utilization in chemical conversion is discussed in detail, linking the physical effects of cavitation and the followup chemical transformations.

The next three chapters (Chapters 6, 7, and 8) deal with the engineering translation of the basic physical and chemical concepts discussed in Chapters 1 to 5 into their possible practical uses. Various designs reported in the literature using hydrodynamic, acoustic, or laser energy for the generation of cavitation are discussed in terms of operational and design difficulties and ease of the chemical transformation. New, probable, and/or novel reactor configurations have also been proposed. Specific examples have been selected to highlight the difficulty or the ease of operation of various types of cavitation reactors. Examples have been used with the results to discuss the efficacy of one type of cavitation compared with another. The effect of physicochemical properties and the optimum use of cavitation for the required chemical effects are also discussed.

In these chapters, the problems associated with energy efficiencies and scaleup are also discussed. It has been found that the industrial success of cavitation reactors and their design and optimization strategies differ from system to system or are system specific. The optimization of the cavitation reactor as required for any one system is not necessarily applicable to other systems. The specific parameters responsible for the success of this optimization are highlighted. Some new reactors for specific applications are proposed. These chapters are expected to generate curiosity and research interest in the people working in the field of cavitation chemistry and cavitation reactors.

Chapter 7 deals with mathematical models for cavitation reactors. This subject is very difficult because of the lack of appropriate experimental data, the complexity of the system, and the difficulty in predicting a reactor's behavior at different scales. Numerous models based on different sets of assumptions for the reaction zone are described. Probability density function is used to illustrate the behavior of the reaction zone in an acoustic cavitation reactor.

The cost effectiveness of a cavitation reactor depends very strongly upon the energy efficiency of the steps leading to the chemical transformation. The energy efficiency of the cavity implosion process as a function of frequency is discussed in Chapter 8. The range of frequency covers all types of processes and reactors, such as hydrodynamic (low frequency), acoustic (medium frequency), and laser (high frequency) cavitation. The performance of the acoustic reactor is also evaluated based on the concept of sonochemical yield, an empirical parameter that can help in comparing and evaluating the performance of various types of acoustic reactors.

Chapter 8 also uses concepts discussed in earlier chapters for the design and optimization of a cavitation reactor. It briefly presents some economic comparisons of a few standard effluent treatment and recovery techniques with new techniques

of cavitation-based chemical conversions. Both capital and the operating costs of conventional and nonconventional hydrodynamic, acoustic, and other types of cavitation reactors are briefly discussed. The need for further research is delineated. The chapter first deals with the efficiency of the energy conversion supplied for the global cavitation effect and then the optimized cavitation effect, i.e., the one required for a specific chemical or physical conversion. The results are illustrated with case studies.

Finally, Chapter 9 describes some pilot and large-scale applications of the cavitation chemical transformations. The examples clearly illustrate the commercial viability of the concept discussed in this monograph. While the examples are largely for a hydrodynamic cavitation process because of its favorable economics, a similar development for acoustic cavitation should appear in the near future. Commercial applications for laser and particle cavitations may require more development to make these technologies more economical.

Cavitation reaction engineering is rapidly changing, largely because of its ease of application to a variety of chemical reactions. It is hoped that this monograph summarizes the state of knowledge available on this subject and will fuel more momentum for research in this area. It is our hope that with increased knowledge of the subject, the present "Edisonian" approach will be replaced by a more scientific assessment of the possibilities and applications of cavitation processes.

A monograph such as this would not have been possible without the support of many people. We would like to thank Profs. Luss, Doraiswamy, Sharma, and Joshi for their constant encouragement on this project. One of the authors (ABP) would like to acknowledge the University Grants Commission and the Department of Science and Technology, Government of India for giving him the opportunity to work in this exciting field. We would also like to thank our students, in particular Parag Gogate, Nilesh Vichare and Prashant Tatake for their assistance and comments on the manuscript. Our sincere thanks to Mrs. Melody Land for all the hard and painstaking detail work she carried out for the completion of this project. Our thanks also to Mr. Ron Baker for his help with the drawings. Finally, and most importantly, projects such as this cannot be completed without the love and support of our wives, Mary and Anala, and our children.

CONTENTS

1. Sources and Types of Cavitation

1.1. Introduction	1
1.2. Hydrodynamic Cavitation	3
1.2a. Cavitation Number	4
1.3. Acoustic Cavitation	8
1.4. Optic and Particle Cavitation	14

2. Cavitation Bubble Dynamics

2.1. Introduction	15
2.2. Bubble Dynamics	16
2.2a. Bubble Nuclei: Blake Threshold	17
2.2b. Dynamic Equations of a Spherical Bubble: Analysis of an Empty Bubble	20
2.2c. Dynamics of a Gas Bubble	21
2.2d. Equation Involving Compressibility of a Liquid	24
2.2e. Rayleigh Analysis of a Cavity and Its Extensions	26
2.2f. Adiabatic Collapse of a Gas-Filled Cavity	28
2.2g. Damping of Stable Bubbles	30
2.2h. Modifications for Hydrodynamic Cavitation	33
2.3. Cluster Dynamics	36
2.3a. Model Equations for Cluster Dynamics	37
2.4. Heat and Mass Transfer Effects in Cavitation	39
2.4a. Rectified Diffusion	39
2.4b. Rectified Heat Transfer in Bubble Oscillations	47
2.4c. Effect of Simultaneous Diffusion and Evaporation on Bubble Dynamics	50
2.5. Concluding Remarks	54

3. Factors Affecting Cavitation Behavior

3.1. Introduction	55
3.2. Factors Affecting Cavity Behavior in Hydrodynamic Cavitation	55
3.2a. Recovered Discharge Pressure and Time of Pressure Recovery . .	57
3.2b. Downstream Pipe Size	62
3.2c. Orifice-to-Pipe Diameter Ratio	62
3.2d. Initial Bubble Radius and the Noncondensable Gas Fraction in Cavitating Liquids	62
3.3. Factors Affecting Cavity Behavior in Acoustic Cavitation	66
3.3a. Acoustic Frequency	66
3.3b. Acoustic Intensity	72
3.3c. External Pressure	72
3.3d. Nature of the Dissolved Gas	73
3.3e. Physical Properties of the Cavitating Medium	74
3.3f. Pretreatment of the Liquid	74
3.3g. Bulk Liquid Temperature	74
3.3h. Initial Bubble Radius	74
3.4. Factors Affecting Optical Cavitation	75
3.5. Factors Affecting Cavity Cluster Behavior in Hydrodynamic Cavitation	77
3.5a. Effect of Recovery Pressure	78
3.5b. Effect of Time of Pressure Recovery	78
3.5c. Effect of Initial Cluster Radius	78
3.5d. Effect of Bubble Volume Fraction	80
3.6. Factors Affecting Cavity Cluster Behavior in Acoustic Cavitation	81
3.7. Concluding Remarks	82

4. Gas-Liquid Cavitation Chemistry

4.1. Introduction	85
4.2. Mechanisms for Cavitation Reaction	90
4.3. Factors Affecting Cavitation Chemistry	96
4.3a. Acoustic Frequency	96
4.3b. Acoustic Intensity	98
4.3c. External Pressure	99
4.3d. Gas Solubility	101
4.3e. Nature of the Gas	101
4.3f. Liquid Properties	102
4.3g. Bulk Temperature	104
4.4. Inorganic and Organic Cavitation Reactions	106
4.4a. Water	107
4.4b. Effect of Other Dissolved Gases	110
4.4c. Inorganic Reactions	112
4.4d. Organic Reactions	116
4.4e. Solute Hydrophobicity and Reactivity	136

4.5.	Depolymerization and Repolymerization Reactions	142
4.6.	Ultrasound and Homogeneous Oxidation	149
4.7.	Ultrasound and Liquid-Liquid Phase-Transfer Reactions	151
 5. Gas-Liquid-Solid Cavitation Chemistry		
5.1.	Introduction	155
5.2.	General Effects of Ultrasound on Gas-Liquid-Solid Reactions	160
5.2a.	Surface Cleaning	160
5.2b.	Morphological Changes in Metal Catalysts	162
5.2c.	Cavitation Erosion	162
5.2d.	Shape, Size, and Specific Area of Particle	163
5.2e.	Improved Mass Transport	163
5.2f.	Mechanisms for Gas-Liquid-Solid Cavitation Reaction	164
5.3.	Specific Role of Ultrasound on Gas-Liquid-Solid Reactions	165
5.3a.	Catalyst and Reagent Preparation	165
5.3b.	Effects of Ultrasound on Catalyst-Reagent Activation	172
5.3c.	Catalyst Induction Period	176
5.3d.	Reactions with Continuous Ultrasound	177
5.3e.	Effects of Ultrasound on Catalyst Regeneration	178
5.4.	Case Studies	179
5.4a.	Cavitation Effect on Heterogeneous Catalytic Oxidation	179
5.4b.	Cavitation Effect on Liquid-Solid Phase-Transfer Reactions	183
5.4c.	Cavitation Effect on Gas-Liquid-Solid Biological Reactions	185
5.4d.	Cavitation Effect on Photo-oxidation Reactions	188
5.4e.	Cavitation-Induced Microfusion	190
 6. Cavitation Reactors		
6.1.	Introduction	193
6.2.	Hydrodynamic Cavitation Reactors	194
6.2a.	High-Pressure Homogenizer	197
6.3.	Acoustic Cavitation Reactors	198
6.3a.	Transducers and Horns	201
6.3b.	Measurements of Acoustic Power	204
6.3c.	Methods for Measuring Amplitude	206
6.3d.	Hydrophones	207
6.3e.	Sonochemical Reactor Geometries	208
6.3f.	Qualitative Considerations for Reactor Choice, Scaleup, and Optimization	238
6.4.	Laser Cavitation Reactors	240
6.5.	Some Additional Considerations for Flow Reactors	243
6.6.	Health and Safety Aspects of Laboratory Reactors	244
6.7.	Integration of Cavitation into Existing Scaled-Up Processes	245
6.8.	Concluding Remarks	245

7. Models for Cavitation Reactors

7.1. Introduction	247
7.2. General Considerations for a Gas–Liquid Cavitation Reactor Model . .	248
7.2a. Bubble Dynamics	249
7.2b. Pyrolysis Reactions in the Bubble	249
7.2c. Free Radical Reactions in the Liquid Film	250
7.3. Modeling a Batch Gas–Liquid Acoustic Reactor	252
7.3a. Physical Description	253
7.3b. Model Equations and Analysis	254
7.3c. Further Improvements in the Model	262
7.4. Characterization of the Reaction Zone	264
7.4a. Physical Description	265
7.4b. Reaction Zone based on Probability Density Function	267
7.5. Reactor Design and Scaleup based on the Concept of Cavitation Yield . . .	272
7.6. Memory Effect in a Loop Cavitation Reactor	273
7.7. Concluding Remarks	275

8. Energy Efficiency and the Economics of the Cavitation Conversion Process

8.1. Introduction	277
8.2. Efficiency of Energy Transformation	279
8.2a. Steps for Energy Transformation	279
8.2b. Equipment Efficiency	280
8.2c. Energy Efficiency for the Cavity Implosion	280
8.2d. Cavitation Yield Model	293
8.2e. G-Method for Energy Efficiency	304
8.2f. Case Studies	305
8.3. Economics of Cavitation Conversion Processes	307
8.3a. Case Study 1	307
8.3b. Case Study 2	310
8.3c. Sonochemistry vs. Photochemistry	311
8.4. Concluding Remarks	312

9. CAV-OX Process

9.1. Introduction	313
9.2. Description of Process	313
9.3. Process Economics	319
9.4. Case Studies	321
Case 1. Superfund Site for Wood-Treatment, Pensacola, Florida	322
Case 2. Chevron Service Station, Long Beach, California	323
Case 3. Presidio Army Base, San Francisco, California	323
Case 4. Chemical Plant, East Coast, United States	326
Case 5. Mannesmann Anlagenbau, Salzburg, Austria	327
Case 6. Steel Mill, South Korea	327
Case 7. Perdue Farms, Bridgewater, Virginia	328

CONTENTS

xvii

Case 8. Southern California Edison, Los Angeles, California	330
Case 9. Corporacion Mexicana de Investigacion en Materials, S.A. de C.V. (CMIMSA)	331
Case 10. University of Natal, Durban, South Africa	331
Nomenclature	333
References	339
Index	349

CAVITATION REACTION ENGINEERING